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(54) PHOTOGRAPHIC ELEMENTS CONTAINING 2-EQUIVALENT PYRAZOLONE COUPLERS AND PROCESS FOR THEIR USE

PHOTOGRAPHISCHES ELEMENT, 2-AEQUIVALENT PYRAZOLON-KUPPLER ENTHALTEND, SOWIE VERFAHREN ZU DEREN ANWENDUNG

ELEMENTS PHOTOGRAPHIQUES CONTENANT DES COPULANTS DE PYRAZOLONE 2-EQUIVALENTS ET PROCEDE D'UTILISATION

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(56) References cited:
EP-A- 0 081 768
DE-A- 3 625 616
WO-A-91/18323

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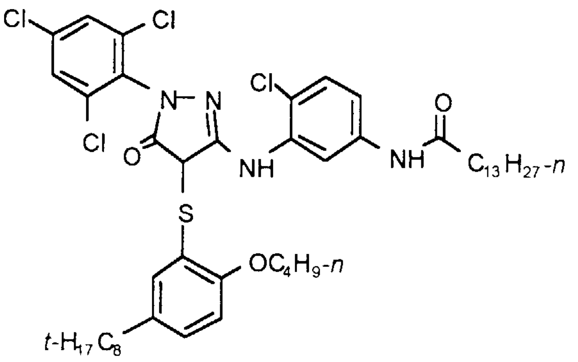
Description

Background of the Invention

This invention relates to pyrazolone magenta dye-forming couplers having a particular thio coupling-off group that enables improved photographic properties and to photographic materials and processes comprising such couplers.

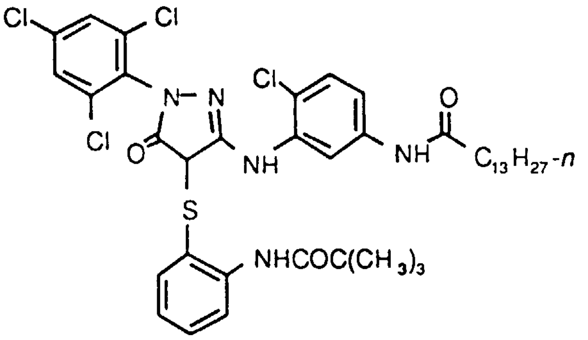
In color photographic silver halide materials and processes pyrazolone couplers comprising arylthio coupling-off groups have provided magenta dye images having useful properties. Examples of such compounds are described in, for example, U.S. Patents 4,413,054, Japanese published patent application 60/057839, U.S. 4,900,657, U.S. 4,351,897 and DE 3625616. An example of such a pyrazolone coupler described in, for example, U.S. Patent 4,413,054 is designated herein as comparison coupler C-1 and is represented by the formula:



C-1

Coupler C-1 has not been entirely satisfactory due to the formation of undesired stain in a color photographic silver halide element upon exposure and processing and because it does not provide the desired image-dye density upon rapid machine processing. The coupler C-1 does not achieve full dye density, especially when the exposed color photographic element is machine processed without the presence of Lippman fine grain silver halide being present in the photographic element. It has been desirable to reduce or avoid the need for added Lippman fine grain silver halide without diminishing dye density in the processed color photographic silver halide element.

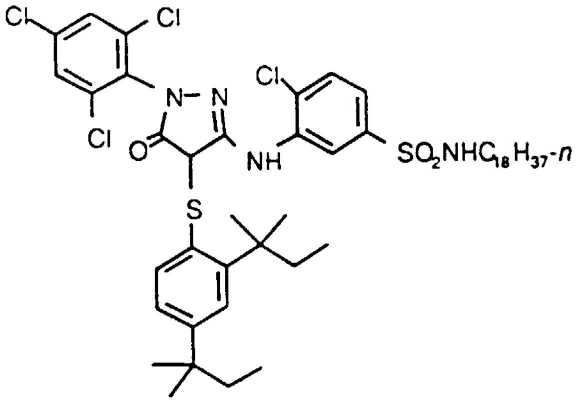
Another example of a pyrazolone coupler known to the art is described in U.S. Patent 4,853,319 is designated herein as comparison coupler C-2 and is represented by the formula:



C-2

The presence of an acylamine group in the ortho position on the phenylthio coupling-off group of coupler C-2 has provided advantageous properties. This coupler does not require Lippman fine grain silver halide in order to obtain adequate dye density upon rapid machine processing. However, the coupling activity of both couplers C-1 and C-2 is unacceptably reduced in the presence of polyvalent cations, especially calcium ion, which leads to a reduction of the color density of the green record. Further, the hue of the resultant dyes from these two couplers is too hypsochromic to give good color reproduction. Another problem of certain types of arylthiopyrazolone couplers is extremely poor solubility in photographic coupler solvents. The poor solubility necessitates the use of auxiliary solvents which then have to be removed through an undesirable additional washing step. U.S. Patent 4,942,116, to Renner (Counterpart to DE 3,730,557) teaches 3 anilino pyrazolones with a broad array of arylthio coupling-off groups containing an alkyl substituent in the ortho position. The products are, however, concerned with light stability of dye images in color prints and not the features described for this invention. Moreover, the only examples that provide a sigma of 1.3 as provided for herein utilize cyanide as an electron withdrawing agent. Cyanide substituents are not within this invention because of their notorious light instability (see for example EP 439,069).

U.S. 4,740,438 teaches the use of organic disulfides as image dye light stabilizers with couplers such as C-10. This type of coupler is characterized by having a 5-sulfamoyl ballast in the 3-anilino ring of the pyrazolone. This type of coupler shows extremely poor light stability in the white areas of photographic prints, and exposure of the print to light leads to unacceptable yellowing in areas of minimum density.



C-10

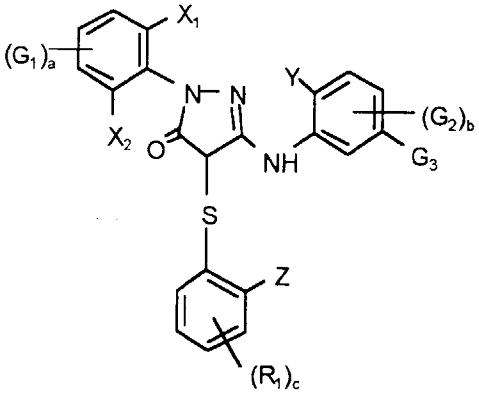
Another type of coupler that has been considered is one having a pentachloro- substitution on the N phenyl ring (U.S. Patent No. 4,876,182). While such materials provide advantageous properties they are not preferred because rings containing more than 3 chloro substituents present laborious and costly administrative efforts relative to disposal.

PCT Publication No. WO 91/18323 discloses the use of a phenylpyrazolone magenta coupler in combination with a substituted phenol in a photographic material to provide enhanced light stability of the resultant magenta image dye.

It has been desired to provide a new pyrazolone coupler having an arylthio coupling-off group in a color photographic silver halide element and process which is capable of forming a magenta dye image of good dye hue and stability, with high dye yield based on rapid machine processing, and with reduction or omission of Lippman fine grain silver halide in the element. Also, it has been desired to provide such 2-equivalent pyrazolone couplers with adequate solubility/ dispersibility characteristics, so that the couplers can be easily incorporated into color photographic silver halide elements. Further, it has been desired to reduce the sensitivity of arylthiopyrazolone couplers toward changes in polyvalent cation levels, especially calcium ion, in the processing of photographic elements. Additionally, it has been desired to provide such a coupler which enables a dye after exposure and processing that displays excellent thermal stability.

Summary of the Invention

It has now been found that superior photographic properties are provided by a photographic element comprising at least one photosensitive silver halide emulsion layer having associated therewith a 5-pyrazolone photographic coupler represented by the formula:



wherein:

a) substituents X_1, X_2, Y, G_1 and G_2 are individually selected from the group consisting of halogen, alkyl, alkoxy, aryloxy, acylamino, alkylthio, arylthio, sulfonamido, sulfamoyl, sulfamido, carbamoyl, diacylamino, alkoxycarbonyl, aryloxycarbonyl, alkoxysulfonyl, aryloxysulfonyl, alkylsulfonyl, arylsulfonyl, alkylsulfinyl, arylsulfinyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, acyloxy, nitro, trifluoromethyl and carboxy and, in the case of X_1, X_2, and Y, hydrogen;

b) a, b, and c are individually integers form 0 to 3 provided that "a" cannot be an integer which, combined with the selection of X_1 and X_2, allows the number of chloride substituents on the ring containing G_1 to exceed 3;

c) G_3 is selected from the group consisting of hydrogen, halogen, acylamino, sulfonamido, sulfamido, carbamoyl, diacylamino, alkoxycarbonyl, aryloxycarbonyl, alkoxysulfonyl, aryloxysulfonyl, alkylsulfonyl, arylsulfonyl, alkylsulfinyl, arylsulfinyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, acyloxy, trifluoromethyl and carboxyl;

d) R_1 is selected from the group consisting of G_1 and hydroxyl;

e) Z is an alkyl group containing at least 3 carbon atoms; and

f) the sum of the sigma values for X_1, X_2, Y, G_1, G_2, and G_3 is at least 1.3, preferably at least 1.4.

Detailed Description of the Invention

Examples of G_1, G_2, X_1, X_2, Y, and R_1 include halogen, such as chlorine, bromine or fluorine; alkyl, including straight or branched chain alkyl, such as alkyl containing 1 to 30 carbon atoms, for example methyl, trifluoromethyl, ethyl, *t*-butyl, and tetradecyl; alkoxy, such as alkoxy containing 1 to 30 carbon atoms, for example methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy 2-(2,4-di-*t*-pentylphenoxy) ethoxy, and 2-dodecyloxyethoxy; aryloxy, such as phenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; acylamino, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-*t*-pentylphenoxy)acetamido, alpha-(2,4-di-*t*-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)hexanamido, alpha-(4-hydroxy-3-*t*-butylphenoxy) tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecyl-pyrrolin-1-yl, N-methyl-tetradecanamido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-toluylsulfonamido, *p*-dodecyl-benzenesulfonamido, N-methyltetradecylsulfonamido, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-hexadecylsulfamoyl, N, N-dimethylsulfamoyl; N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-*t*-pentylphenoxy) butyl]-sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; sulfamido, such as N-methylsulfamido and N-octdecylsulfamido; sulfamido, such as methylsulfamido, phenylsulfamido, *p*-toluylsulfamido, *p*-dodecylphenylsulfamido, N-methyltetradecylsulfamido, and hexadecylsulfamido; carbamoyl, such as N-methylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctyl-carbamoyl; diacylamino, such as N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino; aryloxycarbonyl, such as phenoxycarbonyl and *p*-dodecyl-oxyphenoxycarbonyl; alkoxycarbonyl, such as alkoxycarbonyl containing 2 to 30 carbon atoms, for example methoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, and dodecyloxycarbonyl; alkoxysulfonyl, such as alkoxysulfonyl containing 1 to 30 carbon atoms, for example methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, and 2-ethylhexyloxysulfonyl; aryloxysulfonyl, such as phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl; alkylsulfonyl, such as alkylsulfonyl containing 1 to 30 carbon atoms, for example methylsulfonyl, octylsulfonyl, 2-ethylhexyl-sulfonyl, and hexadecylsulfonyl; arylsulfonyl, such as phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-toluylsulfonyl; alkylsulfinyl, such as alkylsulfinyl containing 1 to 30 carbon atoms, for example methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl,and hexadecylsulfinyl; arylsulfinyl, such as phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-toluylsulfinyl; alkylthio, such as alkylthio containing 1 to 22 carbon atoms, for example ethylthio, octylthio, benzylthio, tetradecylthio, and 2-(2,4-di-*t*-pentylphenoxy)ethylthio; arylthio, such as phenylthio and *p*-tolylthio; alkoxycarbonylamino, such as ethoxycarbonylamino, benzyloxycarbonylamino, and hexadecyloxycarbonylamino; aryloxycarbonylamino, such as phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl) carbonylamino, and *p*-dodecylphenylcarbonylamino, and *p*-toluylcarbonylamino; alkylureido, such as N-methylureido, N, N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N, N-dioctadecylureido, and N, N-dioctyl-N'-ethyl-ureido; arylureido, such as N-phenylureido, N, N-diphenylureido, N-phenyl-N-*p*-toluylureido, N-(*m*-hexadecylphenyl)ureido,and N, N-(2,5-di-t-pentylphenyl)-N'-ethyl-ureido; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamido benzoyloxy, and cyclohexylcarbonyloxy; nitro; carboxy (-COOH); and except for G_1, G_2, and R_1, hydrogen.

Preferably the sum of the sigma values for X_1, X_2, Y, G_1, G_2, and G_3 is at least 1.4.

G_3 is suitably selected from hydrogen, halogen, acylamino, sulfonamido, sulfamido, carbamoyl, diacylamino, alkoxycarbonyl, aryloxycarbonyl, alkoxysulfonyl, aryloxysulfonyl, alkylsulfonyl, arylsulfonyl, alkylsulfinyl, arylsulfinyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, acyloxy, trifluoromethyl and carboxyl with suitable specific examples of each group as specified above for G_2.

Among the compounds described above, a preferred embodiment is represented by the above formula wherein the substituents X_1, X_2, Y, G_1 and G_2 are individually selected from the group consisting of chloride, fluoride, acylamino, sulfonamido, sulfamoyl, carbamoyl, alkoxycarbonyl, aryloxycarbonyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, and trifluoromethyl.

A particularly preferred embodiment is represented by the above formula wherein the substituents X_1, X_2, and Y are chloride, and G_1 and G_2 are individually selected from the group consisting of chloride, fluoride, acylamino, sulfonamido, sulfamoyl, carbamoyl, alkoxycarbonyl, aryloxycarbonyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, and trifluormethyl.

Preferably Z is an alkyl group of not more than 30 carbon atoms, preferably less than 20 carbon atoms. Moreover c is preferably at least 1 and R_1 is an alkyl group, more preferably a branched alkyl group, having at least 3 carbon atoms and in particular preferably not an alkoxy group.

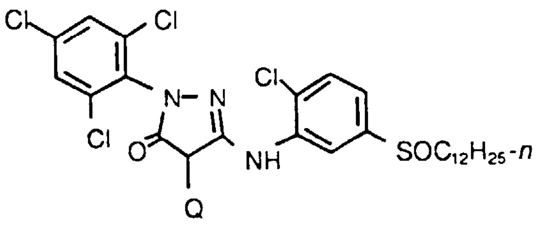
Further, in the preferred embodiment, the substituent Z is also a branched alkyl group containing at least three carbon atoms and the total number of carbon atoms in Z and R_1 sum to at least 6 carbon atoms.

In a most preferred embodiment, substituents X_1, X_2, Y, and G_1 are chloride, "a" is equal to 1 and G_1 is para to the pyrazolone ring, and G_2 is selected from the group consisting of chloride, fluoride, acylamino, sulfonamido, sulfamoyl, carbamoyl, alkoxycarbonyl, aryloxycarbonyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, and trifluormethyl, provided that the sum of the sigma values for X_1, X_2, Y, G_1 and G_2 is at least 1.3.

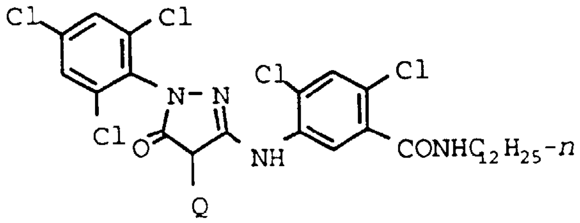
The term "coupler" herein refers to the entire compound, including the coupler moiety and the coupling-off group. The term "coupler moiety (COUP)" refers to that portion of the compound other than the coupling-off group.

The coupler moiety (COUP) can be any 3-anilinopyrazolone coupler moiety useful in the photographic art to form a color reaction product particularly a magenta dye, with oxidized color developing agent provided the substituents meet the requirements above described. Useful pyrazolone coupler moieties are described in, for example, U.S. 4,413,054; U.S. 4,853,319; U.S. 4,443,536; U.S. 4,199,361; U.S. 4,351,897; U.S. 4,385,111; Japanese Published Patent Application 60/170854; U.S. 3,419,391; U.S. 3,311,476; U.S. 3,519,429; U.S. 3,152,896; U.S. 2,311,082; and U. S. 2,343,703; the disclosures of which are incorporated herein by reference. The coupling-off group, if any, on the pyrazolone coupler moiety described in these patents or patent applications can be replaced by a coupling-off group according to the invention. The pyrazolone coupler according to the invention can be in a photographic element in combination with other magenta couplers known or used in the photographic art, such as in combination with at least one of the pyrazolone couplers described in these patents or published patent applications of the invention. The COUP portion of the couplers can be obtained as is known to the art. For example, syntheses of COUP moieties are described in Item 16736 in Research Disclosure, March 1978; U.K. Patent Specification 1,530,272; U.S. 3,907,571; and U.S. 3,928,044.

Illustrative couplers include:



A-1



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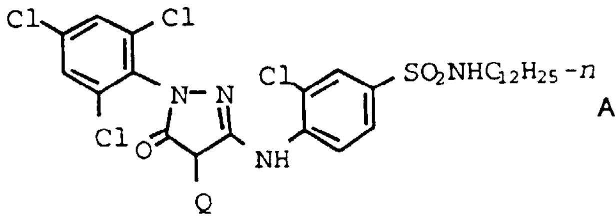
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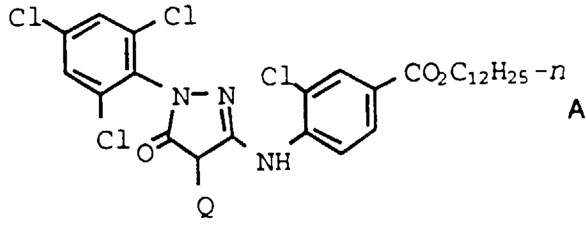
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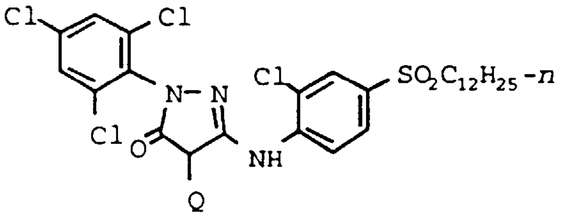
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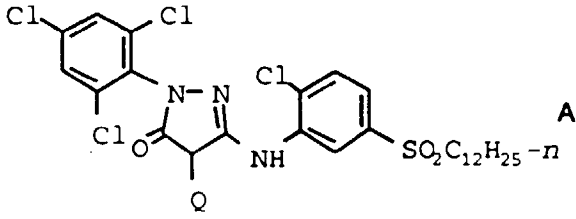
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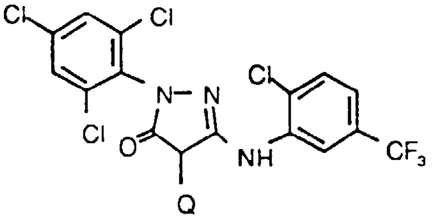
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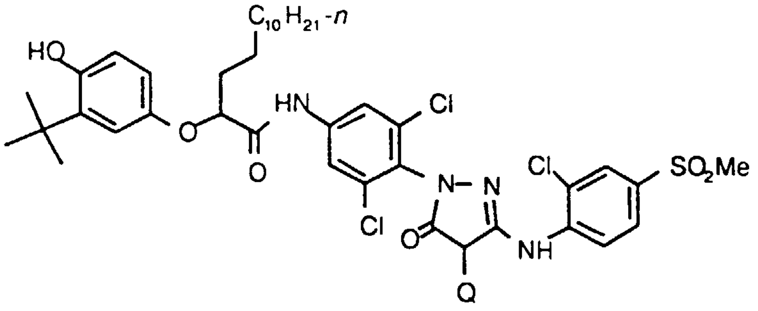
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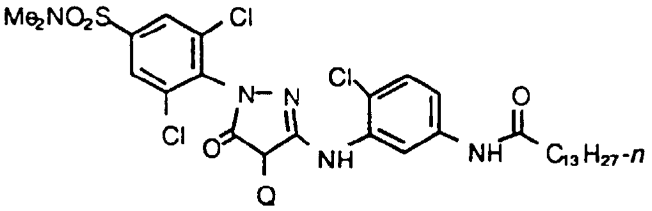

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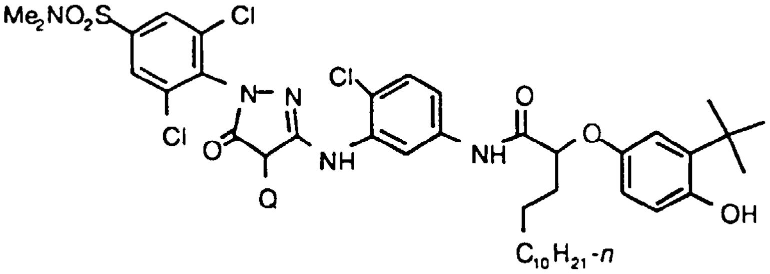

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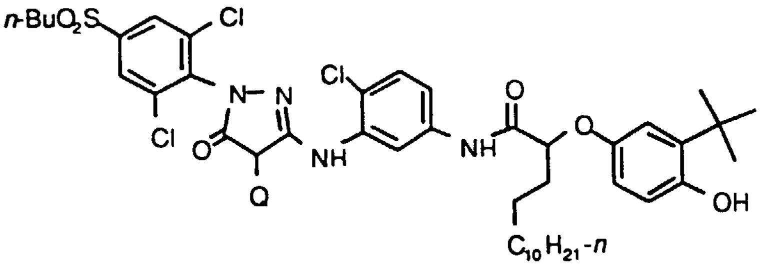

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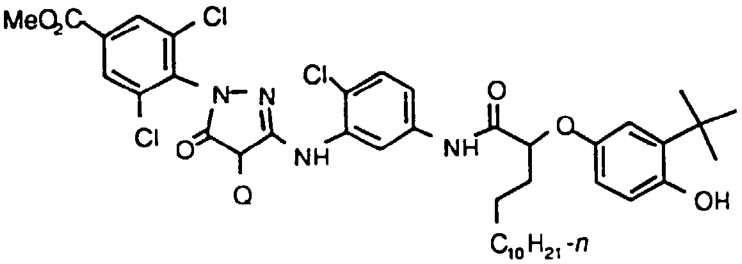

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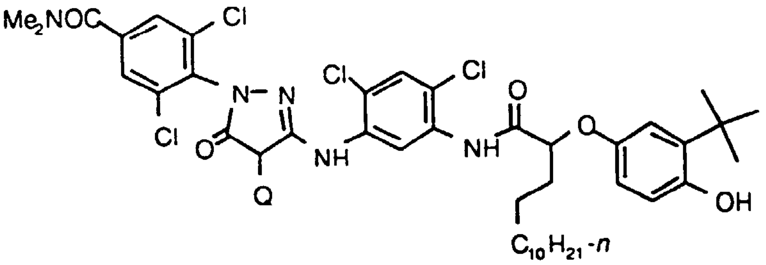
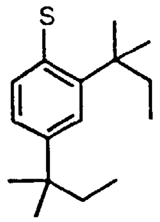


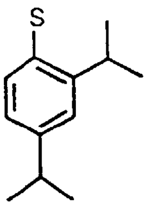
A-13

"**Q**" represents a coupling-off group according to the invention. Substituents that have been used or known on arylthio coupling-off groups on pyrazolone couplers can be used as **Q**. Optional substituents R_1 on this ring include the following: hydroxyl, halogen, alkyl, alkoxy, aryloxy, acylamino, alkylthio, arylthio, sulfonamido, sulfamoyl, sulfamido, carbamoyl, diacylamino, alkoxycarbonyl, aryloxycarbonyl, alkoxysulfonyl, aryloxysulfonyl, alkylsulfonyl, arylsulfonyl, alkylsulfinyl, arylsulfinyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, acyloxy, nitro, trifluoromethyl and carboxy. Examples of these substituents are as specified above for G_1.

Illustrative coupling-off groups (**Q**) are as follows:



Q-1



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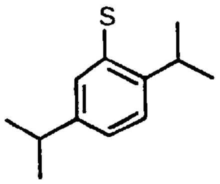

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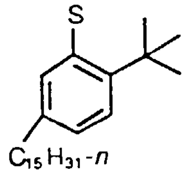

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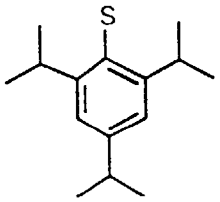

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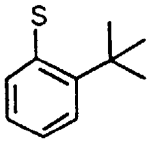

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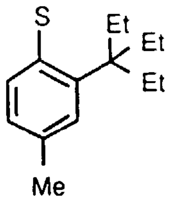

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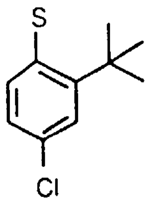

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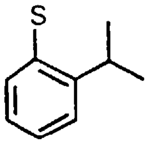

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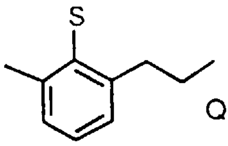

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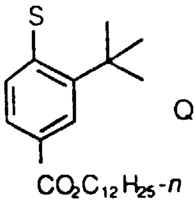

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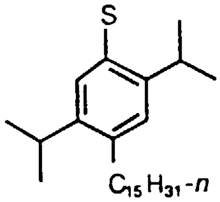

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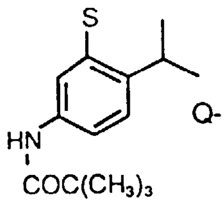
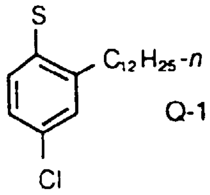
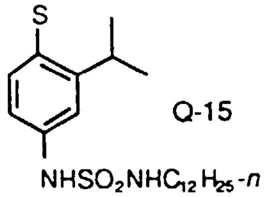


Q-13



Q-14



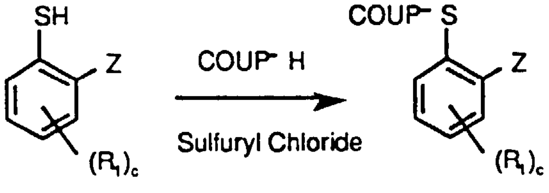
Q-15

The pyrazolone couplers preferably comprise a ballast group. The ballast group can be any ballast known in the photographic art and typically has from 6 to 30 carbon atoms. The ballast is typically one that does not adversely affect reactivity, stability and other desired properties of the coupler of the invention and does not adversely affect the stability, hue and other desired properties of the dye formed from the coupler. Illustrative useful ballast groups are described in the following examples.

Any addenda conventionally employed in conjunction with magenta couplers such as amine stabilizers (e.g. those described in U.S. 5,096,805) are suitably used with these couplers.

Couplers of this invention can be prepared by reacting the parent 4-equivalent coupler containing no coupling-off group with the arylthiol of the coupling-off group according to the invention. This is a simple method and does not involve multiple complicated synthesis steps. The reaction is typically carried out in a solvent, such as dimethylformamide or pyridine.

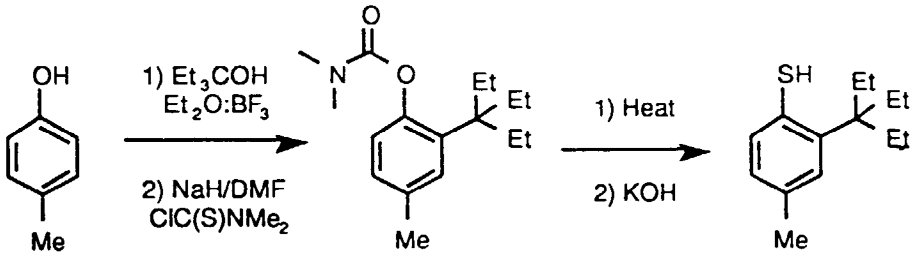
The couplers according to the invention can be prepared by the following illustrative synthetic scheme, where COUP represents the coupler moiety having the coupling-off group attached at its coupling position:



wherein COUP is the coupler moiety and Z and R_1 are as defined.

The following examples illustrate the preparation of couplers of this invention.

Synthesis Example A



Synthesis of Leaving Groups, Synthesis of 2-*tert*-Heptyl-4-methylphenol: The multi-step synthetic sequence described for the synthesis of 2-*t*-heptyl-4-methylbenzenethiol is representative. An oven-dried 1-L flask fitted with a magnetic stirring bar and a pressure-equalizing dropping funnel was charged with 54 g (500 mmol) of *p*-cresol and 3-ethyl-3-pentanol 87.2 g (750 mmol). The flask was immersed in a water bath (~25°C) and the mixture stirred well. Borontrifluorideetherate 106.5 g (750 mmol) was added dropwise through the addition funnel over a period of 50 min. The reaction was monitored by TLC (CH_2Cl_2:EtOAc, 15:1) for the disappearance of *p*-cresol (2.5 h). Then, 250 mL of water was added and the contents heated to reflux to decompose excess BF_3:etherate complex. The mixture was cooled and extracted with ether (3 x 200 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. Removal of solvents on a rotary evaporator yielded a red/brown oil 118.9 g. This was further purified by flash chromatography (CH_2Cl_2:EtOAc, 20:1) to give 2-tert-heptyl-4-methylphenol 77.7 g (76%) as a pale yellow oil. ^1H NMR (ppm): 0.7 [*t*, 9H, $-[CH_2\underline{CH_3}]_3]$, 1.85 [*s*, 6H, $-[\underline{CH_2}CH_3]_3]$, 2.25 (*s*, 3H, Ar-Me), 4.67 (*s*, 1H, -OH), 6.45-7.03 (3H, aromatic).

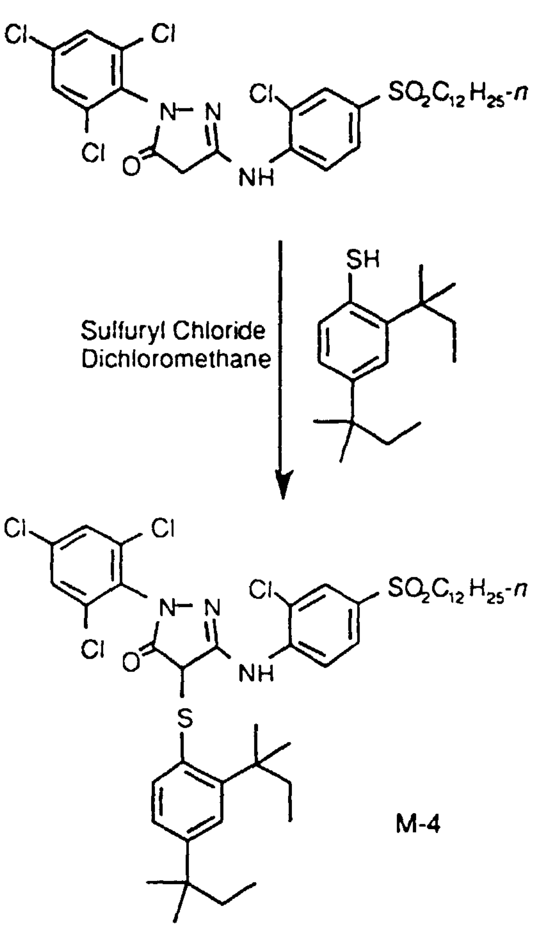
Synthesis of 2-*tert*-Heptyl-4-methylphenyl N,N-dimethyl-O-thiocarbamate: An oven-dried 1-L flask was fitted with a magnetic stirring bar and a pressure-equalizing dropping funnel connected to a mineral oil bubbler and was cooled under a stream of dry argon. The flask was charged with 17.5 g (365 mmol) of 50% sodium hydride dispersed in mineral oil and 150 mL of DMF. To this, well-stirred slurry maintained at 25°C (water bath), 60 g (291 mmol) of 2-tert-heptyl-4-methylphenol dissolved in 150 mL of DMF was added dropwise (1 hr). The mixture was stirred for an additional period of 2.5 hr to complete the formation of the anion. N,N-Dimethylthiocarbamoylchloride 39.5 g (319 mmol) dissolved in 100 mL of DMF was added dropwise to the reaction mixture and monitored by TLC (ligroin 950:EtOAc 5:1). After 1 hr, the mixture was hydrolyzed with dropwise addition of water (35 mL) under argon followed by acidification (100 mL of 2M HCl). The mixture was extracted with 3 x 200 mL portions of ether. Removal of solvents after drying yielded 85 g (100%) of a red oil which on flash chromatography (ligroin 950:EtOAc 6:1) yielded 64 g (75%) of the titled product. ^1H

NMR, ppm: 0.72 [*t*, 9H, $C(CH_2\underline{CH_3})_3$], 1.75 [B, 6H, $-\underline{CH_2}CH_3$ x 3], 2.35 (*s*, 3H, Ar-Me), 3.35 and 3.42 (*s*, 6H, $-NMe_2$), 6.9-7.15 (3H, aromatic).

Thermal Rearrangement of 2-*t*-Heptyl-4-Methylphenyl N,N-Dimethyl-O-thiocarbamate: A 500-mL flask equipped with a magnetic stirring bar and a reflux condenser connected to a mineral oil bubbler was charged with 57.6 g (196 mmol) of 2-*t*-heptyl-4-methylphenyl N,N-dimethylthiocarbamate. The flask was placed over a pre-heated heating mantle (-250°C) and stirred well (25 min). The heating was removed and the contents were allowed to cool. TLC (ligroin 950:EtOAc 5:1) indicated the completion of reaction with some hydrolysis of the rearranged product to free thiol. It was directly used in the next step without further purification.

Hydrolysis of 2-*t*-Heptyl-4-Methylphenylthio-N N-dimethylcarbamate to 2-*t*-Heptyl-4-Methylbenzenethiol (O-7): To the reaction mixture obtained in the previous reaction was added 110 mL of THF and 24.8 g (440 mmol) of potassium hydroxide dissolved in 100 mL of methanol. The mixture was stirred for 1.5 hr at 25°C followed by heating at gentle reflux for 5 hr (completion of hydrolysis). The mixture was poured into crushed ice containing hydrochloric acid and extracted with 3 x 100 mmol portions of ether, washed with brine and dried ($MgSO_4$). Removal of solvent yielded a brown oil which on flash chromatography yielded 38.7 g (89%) of 2-*t*-heptyl-4-methylbenzenethiol (Q-7). This was found to be essentially pure and further purified by distillation, bp 95°C (0.2 mm) to give a clear liquid. ^1H NMR, ppm: 0.72 [*t*, 9H, $-(CH_2\underline{CH_3})_3$], 1.95 [*q*, 6H, $-(\underline{CH_2}CH_3)_3$], 2.3 (*s*, 3H, $Ar-CH_3$), 3.54 (*s*, 1H, -SR). 6.8-7.2 (3H, aromatic). Anal. calcd. for $C_{14}H_{22}S$: C, 75-61; H, 9.97; S, 14.42. Found: C, 75.5; H, 9.9; S, 14.2.

Synthesis Example B: Synthesis of Coupler M-4.

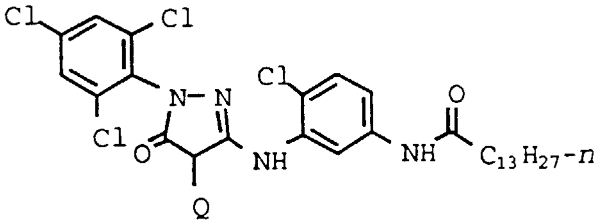


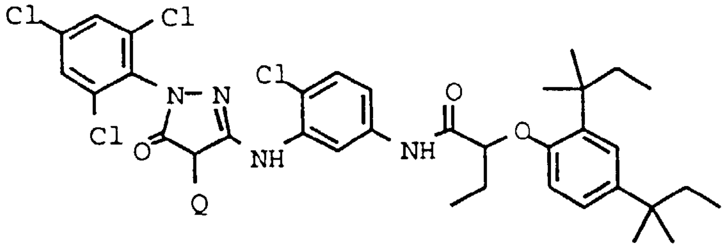
Synthesis of ArSCl: Sulfuryl chloride (2.6 g, 19 mmol) was slowly added to a solution of 2,4-di-tert-pentylbenzenethiol (7.51 g, 30 mmol) in dichloromethane (20 mL). After stirring at room temperature for 2 hrs, the volatiles were removed by rotary evaporation below 40 °C.

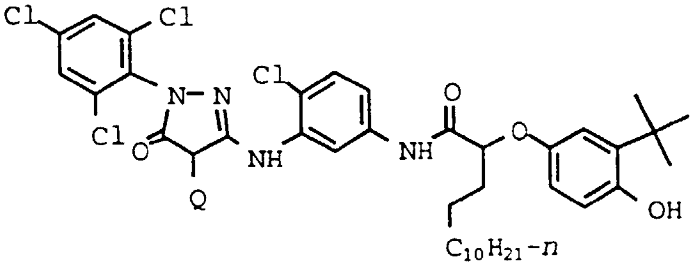
Synthesis of Coupler: A solution of A-5 (Q = H, 11.2 g, 18 mmol) in DMF (50 mL) was added rapidly to the oil obtained above and the resulting solution was stirred at room temperature for 65 hr. The mixture was poured slowly into 3 N HCl (500 mL) and the precipitate was collected by suction filtration. The solid was dissolved in glacial acetic acid (350 mL) and reprecipitated into water. The resulting solid was collected filtration, washed well with water and air dried to give 10.0 g (64 %) of M-4 as a white solid. ^{1}H NMR was consistent with the structure; Anal. calcd. for $C_{43}H_{57}Cl_4N_3O_3S_2$: C, 59.4; H, 6.6; N, 4.8; Cl, 16.3; S, 7.4. Found: C, 58.2; H, 6.5; N, 4.8; Cl 16.1; S, 7.0.

The purity of the two-equivalent couplers synthesized was checked by (a) TLC in two or three different solvent systems of different polarity, (b) HPLC, (c) 270 MHz FT-NMR and (d) elemental analyses (C, H, N, Cl, S); some samples were also subjected to mass spectral analysis.

The following structures are included for comparative purposes:


CA-1


CA-2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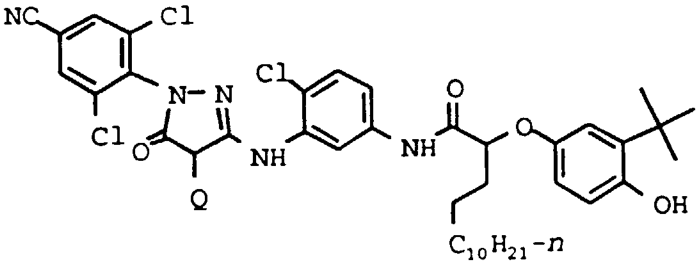
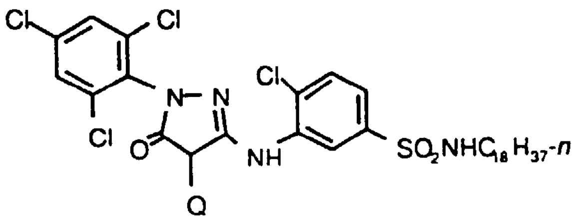
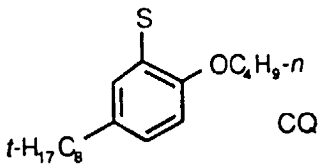
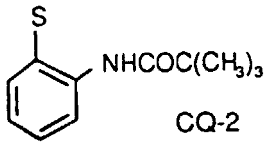

CA-4



CA-5



CQ-1



CQ-2

The following compounds were prepared by this general method:

Table I.

Summary of Couplers									
	HPLC		Elemental Analysis						COUP/Q
Coupler (Type)			C	H	N	Cl	S	mp,°C	
C-1	na	calc.	na					165-167	CA-1/CQ-1
(Check)		found							
C-2	na	calc.	na					129-133	CA-1/CQ-2
(Check)		found							
C-3	96	calc.	62.6	7.0	6.5	3.7		206-208	CA-1/Q-1
(Check)		found	62.2	6.8	6.5	3.7			
C-4	90	calc.	65.6	7.9	5.7	14.3	3.2	174-176	CA-1/Q-4
(Check)		found	65.4	7.7	5.6	14.0	3.1		
C-5	na	calc.	61.9	6.8	6.7	17.0	3.8	230-232	CA-1/Q-7
(Check)		found	61.2	6.7	6.7	17.2	4.0		
C-6	>90	calc.	64.1	6.8	5.9	14.8	3.4	131-134	CA-2/Q-1
(Check)		found	63.9	6.8	5.9	14.4	3.2		
C-7	97	calc.	62.8	6.2	6.2	15.8	3.6	223-223	CA-2/Q-3
(Check)		found	62.9	6.4	6.3	15.1	3.2		
C-8	98	calc.	63.1	6.6	5.8	14.6	3.3	172	CA-3/Q-2
(Check)		found	62.8	6.5	5.6	14.4	3.5		
C-9	96	calc.	61.0	6.5	6.9	17.6	4.0	169-171	CA-1/Q-3
(Check)		found	60.9	6.5	6.9	17.6	4.1		
C-10	98	calc.	60.7	7.3	5.8	14.6	6.4	155-157	CA-5/Q-1
(check)		found	60.7	7.2	5.7	14.6	6.4		
M-1	91	calc.	58.4	6.6	6.3	16.0	7.2	71-75	A-3/Q-1
(Inven.)		found	58.5	6.5	6.2	16.0	6.9		
M-2	96	calc.	56.5	6.1	6.8	17.1	7.7	69-75	A-3/Q-3
(Inven.)		found	56.4	6.1	6.7	17.3	7.6		
M-3	97	calc.	57.5	6.3	6.5	16.5	7.5	decomp	A-3/Q-7
(Inven.)		found	57.6	6.1	6.3	16.2	7.2		
M-4	99	calc.	59.4	6.6	4.8	16.3	7.4	na	A-5/Q-1
(Inven.)		found	58.2	6.5	4.8	16.1	7.0		

Table I. (continued)

Summary of Couplers									
	HPLC		Elemental Analysis						COUP/Q
Coupler (Type)			C	H	N	Cl	S	mp,°C	
M-5	100	calc.	57.6	6.1	5.2	17.4	7.9	na	A-5/Q-2
(Inven.)		found	57.4	6.1	5.1	17.3	7.5		
M-6	95	calc.	57.6	6.1	5.2	17.4	7.9	88	A-5/Q-3
(Inven.)		found	57.4	6.1	5.1	16.5	7.6		
M-7	96	calc.	60.3	6.1	7.5	11.4	6.8	na	A-9/Q-1
(Inven.)		found	60.1	7.0	7.3	10.8	6.6		

Table I summarizes the comparison (C) and invention (M) couplers synthesized for testing. Table II summarizes the sigma values associated with the couplers. Values for sigma were either found in published chemical literature (see for example "The Chemist Companion", A.J. Gordon and R.A. Ford, John Wiley & Sons, New York, 1972; "Progress in Physical Organic Chemistry, Volume 13", R.W. Taft, Ed., John Wiley & Sons, New York; and C. Hansch and A.J. Leo, in "Substituent Constants for Correlation Analysis in Chemisty and Biology", Wiley, New York, 1979), or were calculated using the Medchem program (for a recent discussion of this method see Albert J. Leo, in "Comprehensive Medicinal Chemistry", edited by C. Hansch, P.G. Sammes, and J.B. Taylor, Pergamon Press, New York, Volume 4, 1990). The values for sigma$_{para}$ were used to estimate the value for substituents ortho to the pyrazolone nucleus.

Table II:

Sigma Constant Values							
Coupler	SIGMA			VALUE			Sum of Sigma Values
	X_1	X_2	Y	G_1	G_2	G_3	
C-1	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-2	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-3	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-4	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-5	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-6	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-7	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-8	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-9	0.23	0.23	0.23	0.23	0.00	0.21	1.13
C-10	0.23	0.23	0.23	0.23	0.00	0.46	1.38
M-1	0.23	0.23	0.23	0.23	0.57	0.00	1.49
M-2	0.23	0.23	0.23	0.23	0.57	0.00	1.49
M-3	0.23	0.23	0.23	0.23	0.57	0.00	1.49
M-4	0.23	0.23	0.23	0.23	0.78	0.00	1.64
M-5	0.23	0.23	0.23	0.23	0.78	0.00	1.64
M-6	0.23	0.23	0.23	0.23	0.78	0.00	1.64
M-7	0.23	0.23	0.23	0.57	0.00	0.21	1.47

The couplers of this invention can be used in the ways and for the purposes that couplers are used in the photographic art.

Typically, the couplers are incorporated in silver halide emulsions and the emulsions coated on a support to form a photographic element. Alternatively, the coupler can be incorporated in photographic elements adjacent to the silver halide emulsion where, during development, the coupler will be in reactive association with development products such as oxidized color developing agent. Thus, as used herein, the term "associated therewith" signifies that the coupler is in the silver halide emulsion layer or in an adjacent location where, during processing, the coupler is capable of reacting with silver halide development products.

The photographic elements can be single color elements or multicolor elements. Multicolor elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer, e.g., as by the use of microvessels as described in U.S. Patent No. 4,362,806.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler, at least one of the couplers in the element being a coupler of this invention. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like. In particular it may contain masking material which is yellow in unexposed areas following development. In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, December 1989, Item 308119, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND, which will be identified hereafter by the term "Research Disclosure." The contents of the Research Disclosure, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the Research Disclosure.

The silver halide emulsions employed in the elements of this invention can be either negative-working or positive-working. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through IV. Color materials and development modifiers are described in Sections V and XXI. Vehicles are described in Section IX, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described , for example, in Sections V, VI, VIII, X, XI, XII, and XVI. Manufacturing methods are described in Sections XIV and XV, other layers and supports in Sections XIII and XVII, processing methods and agents in Sections XIX and XX, and exposure alternatives in Section XVIII.

Preferred color developing agents are p-phenylenediamines. Especially preferred are: 4-amino N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N-ethyl-N-(β-(methanesulfonamido) ethyl)aniline sesquisulfate hydrate, 4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate, 4-amino-3-β-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

With negative working silver halide a negative image can be formed. Optionally positive (or reversal) image can be formed.

The magenta coupler described herein may be used in combination with other classes of magenta image couplers such as 3-acylamino-5-pyrazolones and heterocyclic couplers (e.g. pyrazoloazoles) such as those described in EP 285,274; U.S. Patent 4,540,654; EP 119,860, or with other 5-pyrazolone couplers containing different ballasts or coupling-off groups such as those described in U.S. Patent 4,301,235; U.S. Patent 4,853,319 and U.S. Patent 4,351,897. The coupler may also be used in association with yellow or cyan colored couplers (e.g. to adjust levels of interlayer correction) and with masking couplers such as those described in EP 213.490; Japanese Published Application 58-172,647; U.S. Patent 2,983,608; German Application DE 2,706,117C; U.K. Patent 1,530,272; Japanese Application A-113935; U.S. Patent 4,070,191 and German Application DE 2,643,965. The masking couplers may be shifted or blocked.

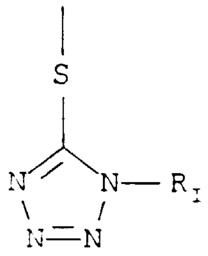
The couplers may also be used in association with materials that accelerate or otherwise modify the processing steps e.g. of bleaching or fixing to improve the quality of the image. Bleach accelerators described in EP 193,389; EP 301,477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784 are particularly useful. Also contemplated is use of the coupler in association with nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; U.K. Patent 2,131,188); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

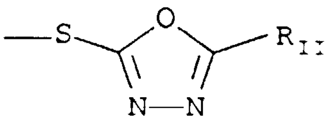
The couplers may also be used in combination with filter dye layers comprising colloidal silver sol or yellow and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. 4,366,237; EP 96,570; U.S. 4,420,556; and U.S. 4,543,323.) Also, the couplers may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. 5,019,492.

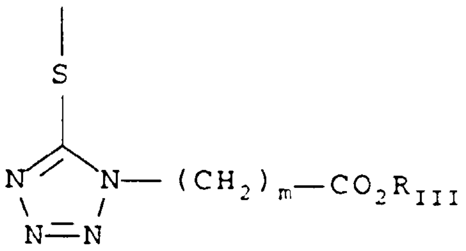
The coupler may further be used in combination with image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIR's). DIR's useful in conjunction with the couplers of the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816;

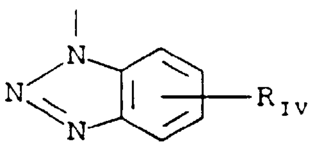
4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063, DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

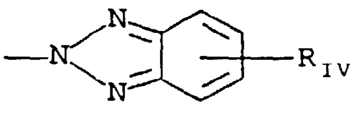
Such compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C. R. Barr, J.R. Thirtle and P.W. Vittum in Photographic Science and Engineering, Vol. 13, p. 174 (1969), incorporated herein by reference. Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) which also include a timing moiety or chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles, benzotriazoles tetrazoles, benzimidazoles, indazoles, isoindazoles, mercaptotetrazoles, selenotetrazoles, mercaptobenzothiazoles, selenobenzothiazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles, benzodiazoles, mercaptooxazoles, mercaptothiadiazoles, mercaptothiazoles, mercaptotriazoles, mercaptooxadiazoles, mercaptodiazoles, mercaptooxathiazoles, telleurotetrazoles or benzisodiazoles. In a preferred embodiment, the inhibitor moiety or group is selected from the following formulas:







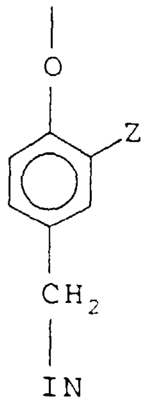


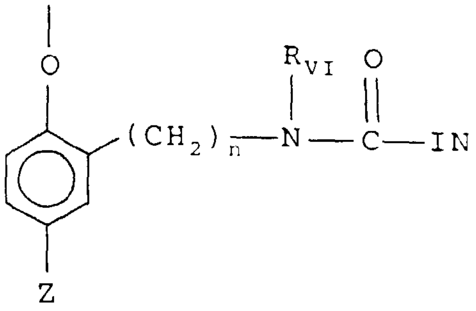


wherein R_I is selected from the group consisting of straight and branched alkyls of from 1 to about 8 carbon atoms, benzyl and phenyl groups and said groups containing at least one alkoxy substituent; R_{II} is selected from R_I and $-SR_I$; R_{III} is a straight or branched alkyl group of from 1 to about 5 carbon atoms and m is from 1 to 3; and R_{IV} is selected from the group consisting of hydrogen, halogens and alkoxy, phenyl and carbonamido groups, $-COOR_V$ and $-NHCOOR_V$ wherein R_V is selected from substituted and unsubstituted alkyl and aryl groups.

Although it is typical that the coupler moiety included in the developer inhibitor-releasing coupler forms an image dye corresponding to the layer in which it is located, it may also form a different color as one associated with a different film layer. It may also be useful that the coupler moiety included in the developer inhibitor-releasing coupler forms colorless products and/or products that wash out of the photographic material during processing (so-called "universal" couplers).

As mentioned, the developer inhibitor-releasing coupler may include a timing group which produces the time-delayed release of the inhibitor group such as groups utilizing the cleavage reaction of a hemiacetal (U.S. 4,146,396, Japanese Applications 60-249148; 60-249149); groups using an intramolecular nucleophilic substitution reaction (U. S. 4,248,962); groups utilizing an electron transfer reaction along a conjugated system (U.S. 4,409,323; 4,421,845; Japanese Applications 57-188035; 58-98728; 58-209736; 58-209738) groups utilizing ester hydrolysis (German Patent Application (OLS) No. 2,626,315; groups utilizing the cleavage of imino ketals (U.S. 4,546,073); groups that function as a coupler or reducing agent after the coupler reaction (U.S. 4,438,193; U.S. 4,618,571) and groups that combine the features describe above. It is typical that the timing group or moiety is of one of the formulas:

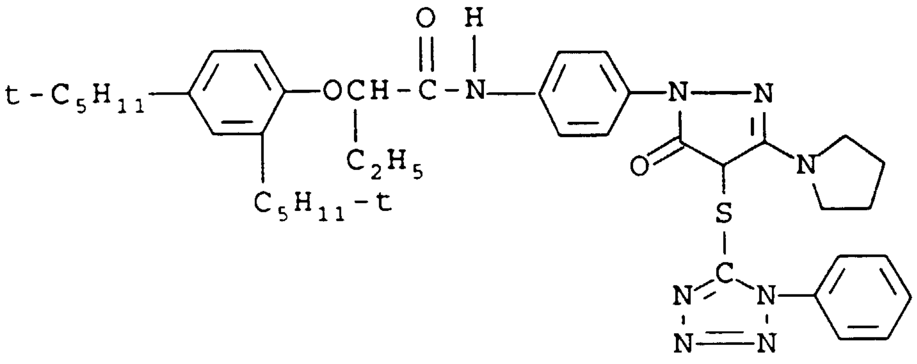




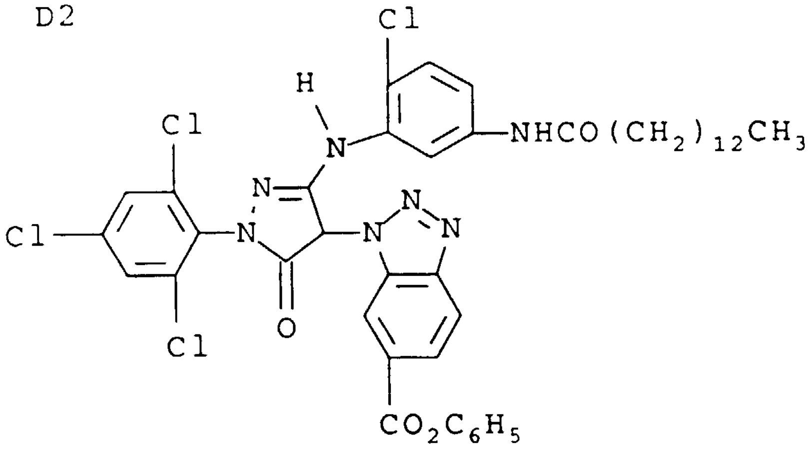
wherein IN is the inhibitor moiety, Z is selected from the group consisting of nitro, cyano, alkylsulfonyl; sulfamoyl ($-SO_2NR_2$); and sulfonamido ($-NRSO_2R$) groups; n is 0 or 1; and R_{VI} is selected from the group consisting of substituted and unsubstituted alkyl and phenyl groups. The oxygen atom of each timing group is bonded to the coupling-off position of the respective coupler moiety of the DIAR.

Suitable developer inhibitor-releasing couplers for use in the present invention include, but are not limited to, the following:

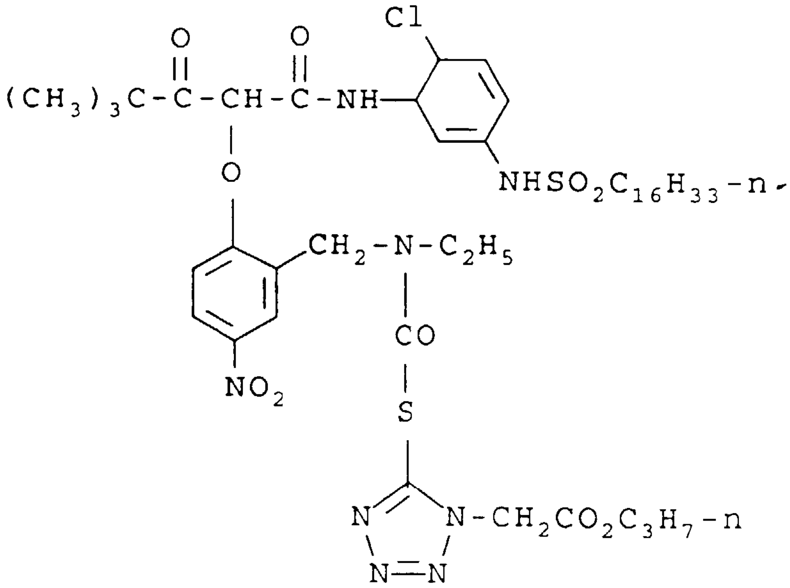
D1



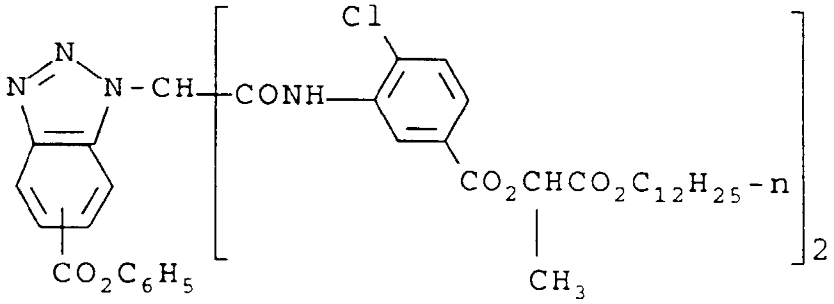
D2



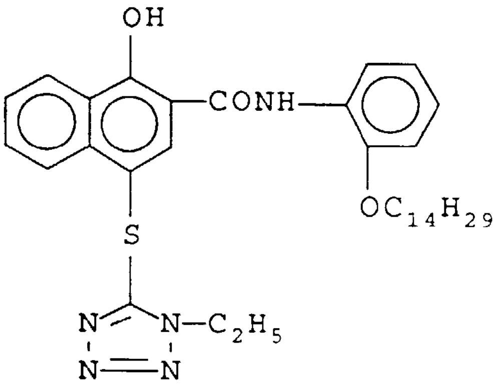
D3



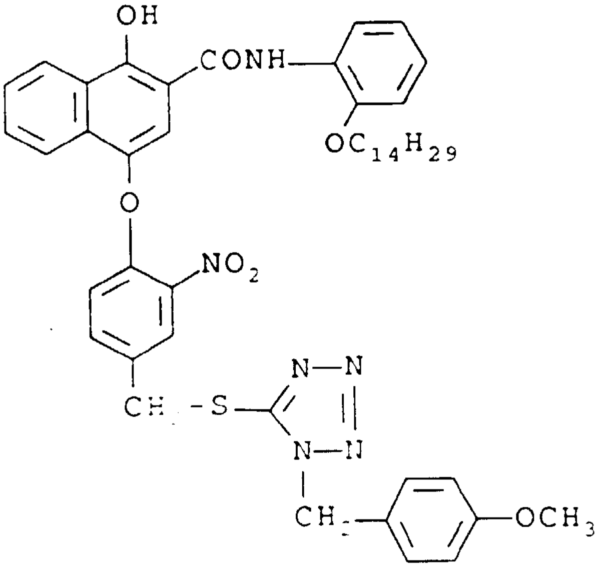
D4


Cl
N
N
N-CH
CONH
$CO_2CHCO_2C_{12}H_{25}$-n
CH_3
$CO_2C_6H_5$
2

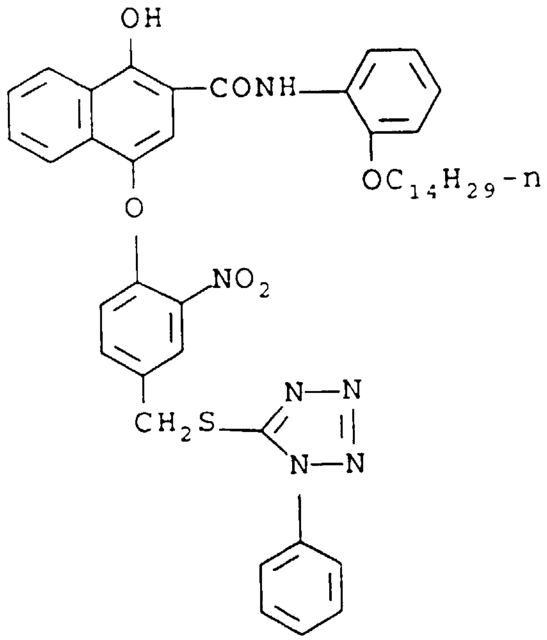
D5


OH
CONH
$OC_{14}H_{29}$
S
N
N-C_2H_5
N
N

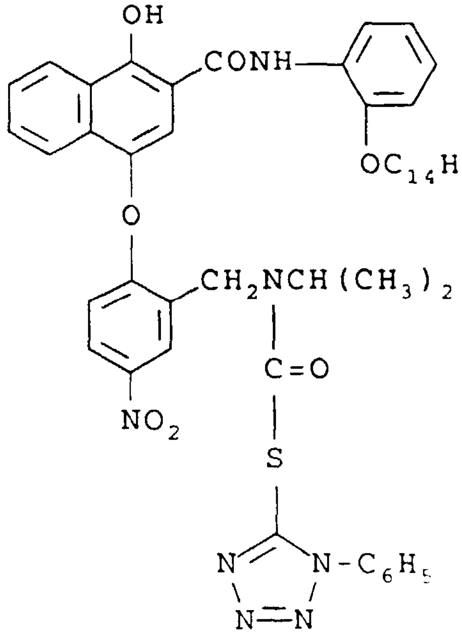
D6


OH
CONH
$OC_{14}H_{29}$
O
NO_2
CH
-S
N
N
N
N
CH
OCH$_3$

D7



D8



It is also contemplated that the concepts of the present invention may be employed to obtain reflection color prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England, incorporated herein by reference. Materials of the invention may be coated on pH adjusted support as described in U.S. 4,917,994; with epoxy solvents (EP 0 164 961); with nickel complex stabilizers (U.S. 4,346,165; U.S. 4,540,653 and U.S. 4,906,559 for example); with ballasted chelating agents such as those in U.S. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium; and with stain reducing compounds such as described in U.S. 5,068,171 and U.S. 5,096,805. Other compounds useful in combination with the invention are disclosed in Japanese Published Applications 83-09,959; 83-62,586; 90-072,629, 90-072,630; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928;

90-086,669; 90-086,670; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,096; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-101,937; 90-103,409; 90-151,577.

Especially useful in this invention are tabular grain silver halide emulsions. Specifically contemplated tabular grain emulsions are those in which greater than 50 percent of the total projected area of the emulsion grains are accounted for by tabular grains having a thickness of less than 0.3 micron (0.5 micron for blue sensitive emulsion) and an average tabularity (T) of greater than 25 (preferably greater than 100), where the term "tabularity" is employed in its art recognized usage as

$$T = ECD/t^2$$

where

ECD is the average equivalent circular diameter of the tabular grains in microns and
t is the average thickness in microns of the tabular grains.

The average useful ECD of photographic emulsions can range up to about 10 microns, although in practice emulsion ECD's seldom exceed about 4 microns. Since both photographic speed and granularity increase with increasing ECD's, it is generally preferred to employ the smallest tabular grain ECD's compatible with achieving aim speed requirements.

Emulsion tabularity increases markedly with reductions in tabular grain thickness. It is generally preferred that aim tabular grain projected areas be satisfied by thin ($t < 0.2$ micron) tabular grains. To achieve the lowest levels of granularity it is preferred to that aim tabular grain projected areas be satisfied with ultrathin ($t < 0.06$ micron) tabular grains. Tabular grain thicknesses typically range down to about 0.02 micron. However, still lower tabular grain thicknesses are contemplated. For example, Daubendiek et al U.S. Patent 4,672,027 reports a 3 mole percent iodide tabular grain silver bromoiodide emulsion having a grain thickness of 0.017 micron.

As noted above tabular grains of less than the specified thickness account for at least 50 percent of the total grain projected area of the emulsion. To maximize the advantages of high tabularity it is generally preferred that tabular grains satisfying the stated thickness criterion account for the highest conveniently attainable percentage of the total grain projected area of the emulsion. For example, in preferred emulsions tabular grains satisfying the stated thickness criteria above account for at least 70 percent of the total grain projected area. In the highest performance tabular grain emulsions tabular grains satisfying the thickness criteria above account for at least 90 percent of total grain projected area.

Suitable tabular grain emulsions can be selected from among a variety of conventional teachings, such as those of the following:

Research Disclosure, Item 22534, January 1983,
published by Kenneth Mason Publications, Ltd.,
Emsworth, Hampshire P010 7DD, England; U.S. Patent Nos. 4,439,520; 4,414,310; 4,433,048; 4,643,966; 4,647,528; 4,665,012; 4,672,027; 4,678,745; 4,693,964; 4,713,320; 4,722,886; 4,755,456; 4,775,617; 4,797,354; 4,801,522; 4,806,461; 4,835,095; 4,853,322; 4,914,014; 4,962,015; 4,985,350; 5,061,069 and 5,061,616.

It is also contemplated that materials of the invention may be employed in conjunction with a photographic material where a relatively transparent film containing magnetic particles is incorporated into the material. The materials of this invention function well in such a combination and give excellent photographic results. Examples of such magnetic films are well known and are described for example in U.S. Patent 4,990,276 and EP 459,349 which are incorporated herein by reference.

As disclosed in these publications, the particles can be of any type available such as ferro- and ferri-magnetic oxides, complex oxides with other metals, ferrites etc. and can assume known particulate shapes and sizes, may contain dopants, and may exhibit the pH values known in the art. The particles may be shell coated and may be applied over the range of typical laydown. The embodiment is not limited with respect to binders, hardeners, antistatic agents, dispersing agents, plasticizers, lubricants and other known additives.

The photographic compositions of the present invention are employed in color photographic materials in a manner well known in the photographic art. For example, a supporting substrate may be coated with a silver halide emulsion and the coupler composition. The photographic material may then be imagewise exposed and then developed in a solution containing a primary aromatic amine color developing agent in a manner well known in the photographic art. As further known in the art, the primary aromatic amine developing agent is oxidized in an imagewise manner by reaction with exposed silver halide grains, and the oxidized developer reacts with coupler to form dye. The development step is followed by bleaching and fixing steps or a bleach-fix step to remove silver and silver halide from the coating.

It is understood thoroughout this specification and claims that any reference to a substituent by the identification of a group containing a substitutable hydrogen (eg alkyl, amine, aryl, alkoxy, heterocyclic, etc.), unless otherwise specifically stated, shall encompass not only the substituent's unsubstituted form but also its form substituted with any photographically useful substituents. Usually the substituent will have less than 30 carbon atoms and typically less than 20 carbon atoms.

The following examples are included for a further understanding of this invention.

Example 1

Solubility and Dispersibility: The solubility was determined by addition of a known weight (0.2 g) of the given coupler to reagent grade ethyl acetate (0.6 g) in a vial and then stirring (5 min) at 25°C. Except for comparison couplers C-3, C-4, and C-5 (all CA-1 derivatives), all couplers dissolved immediately. Couplers C-3 and C-4 were insoluble in 0.6 g of ethyl acetate at 25°C. Additional quantities of ethyl acetate were added in increments to these three couplers. It required 4.5 g of ethyl acetate to dissolve 0.2 g of C-3 and 10.6 g of ethyl acetate to dissolve 0.2 g of C-4. Coupler C-5 (0.2 g) did not show any sign of solubility even after the addition of 10.8 g of ethyl acetate. The dispersibility characteristics of the couplers were determined by gently warming (50°C) these solutions followed by addition of 4 ml of triisopropylnapthalene sulfonate, sodium salt (mixture of isomers) and gel to each vial. The resulting mixture was shaken vigorously and observed for any crystallization. All emulsified except C-3, C-4 and C-5.

These experiments clearly demonstrate the poor solubility/dispersibility characteristics of dialkylarylthio pyrazolones based on comparison parent CA-1. Unlike dialkylarylthio derivatives of CA-1 (C-3, C-4, and C-5), dialkylarylthio derivatives of parents claimed in the invention can be coated without resorting to washed dispersions or dimethylformamide addition. This is a significant and important improvement. While C-10 appears satisfactory in this test, it has unsatisfactory light stability as shown in Table VIII. Table III shows these results.

Table III.

Solubility/Dispersibility of the New Magenta Couplers

Coupler	Type	Solubility	Dispersibility
C-3	Check	Poor	Poor
C-4	Check	Poor	Poor
C-5	Check	Poor	Poor
C-10	Check	Good	Good
M-1	Invention	Good	Good

Example 2

Reduction of Calcium Ion Sensitivity: The coupling kinetics of a number of coupler dispersions with oxidized color developer (4-Amino-3-methyl-N-ethyl-N-(β-methanesulfonamido)ethylaniline sesquisulfatesulfate hydrate,) are determined as a function of the calcium ion concentration by competition with the hydroxide deamination of the oxidized color developer. These competition kinetics are run in a buffer solution (0.0125 M of 4-carboxybenzenesulfonamide) containing a maximum of 0.36 M potassium ion and a series of calcium ion concentrations (from 0 to 0.16 M) with varying potassium ion to maintain a constant total cation level. Known, limited amounts of color developer and excess oxidant (potassium ferricyanide) are added to the dilute dispersions in the buffered media. Tne relative dye yields are determined spectrophotometrically as a function of the coupler concentration. After corrections for interfering densities, the coupling rate constants are calculated from previously determined rates for oxidized developer deamination as a function of pH by use of standard competition kinetics analysis. For each coupler dispersion the log of the coupling rate constant is plotted as a function of the log of the calcium ion concentration. For all of these coupler dispersions there is a region wherein the coupling rate constants are independent of calcium ion concentration (k_1) and a region of decreasing coupling rate with increasing calcium ion concentration. The point of intersection of the calcium ion dependent region and the calcium ion independent region is defined as the threshold, and is reported as the log of the calcium ion concentration for that point. The relative threshold normalizes the values with respect to check coupler C-1. Couplers with a relative threshold of less than 1.0 are more sensitive to calcium ion than couplers with a relative threshold of greater than 1.0. The threshold, the absolute rate constants with no added calcium ion (k_1), at a calcium ion concentration of 0.1 M (k_2), and the difference (Δ log k) are presented in Table IV below. From this information is calculated a relative sensitivity toward calcium ion by normalizing the Δlog k information with respect to check coupler

C-1. Couplers with a relative sensitivity of greater than 1.0 are more sensitive toward calcium ion than couplers with a relative sensitivity of less than 1.0.

As is clearly seen, couplers represented by the invention are less sensitive to the presence of calcium ion in the process than the check couplers. For instance, in comparison to check coupler C-1, invention coupler M-4 has a threshold value 79 times larger, and is more than 4 times less sensitive toward calcium ion at a concentration of 0.1 M.

Table IV.

Relative Reactivity in the Presence of Calcium Ion						
Coupler (Type)	Threshold	Relative Threshold	log k_1	log k_2	Δ log k	Relative Sensitivity
C-1 (check)	-4.3	1.0	2.34	1.22	-1.12	1.0
C-2 (check)	-5.3	0.1	2.90	1.33	-1.57	2.8
C-9 (check)	-4.5	0.6	3.05	1.42	-1.63	3.2
M-2 (Invention)	-2.8	32	3.81	2.84	-0.97	0.71
M-4 (Invention)	-2.4	79	3.11	2.60	-0.51	0.25

Coating Method 1: Photographic elements were prepared by coating a gel-subbed, polyethylene-coated paper support with a photosensitive layer containing a silver chlorobromide emulsion at 0.168 g Ag/m^2 (or 0.337 g for 4-equivalent couplers) gelatin at 1.62 g/m^2, and the magenta image coupler at 0.38 mmol/m^2 dispersed in dibutyl phlthalate (half the weight of the coupler). Each coupler dispersion also contained the following addenda (weight percent of coupler): Addendum-1 (200%), Addendum-2 (10%). The photosensitive layer was overcoated with a protective layer containing gelatin at 1.08 g/m^2 and bisvinylsulfonylmethyl ether hardener at 2 weight percent based on total gelatin.

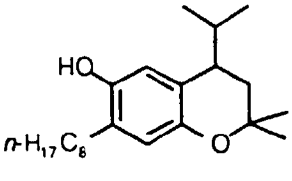
Coating Method 2: Photographic elements were prepared by coating a gel-subbed, polyethylene-coated paper support with a photosensitive layer containing a silver chlorobromide emulsion at 0.172 g Ag/m^2 (or 0.2865 for 4-equivalent couplers), gelatin at 1.238 g/m^2, and a magenta image coupler indicated below at 0.38 mmol/m^2 dispersed in an equal weight of tricresyl phosphate. Each coupler dispersion also contained the following addenda (weight percent of coupler): Addendum-3 (48%), Addendum-4 (29%), Addendum-5 (32%), Addendum-6 (16%).

The photosensitive layer was overcoated with a protective layer containing gelatin at 1.08 g/m^2 and bisvinylsulfonylmethyl ether hardener at 2 weight percent based on total gelatin.

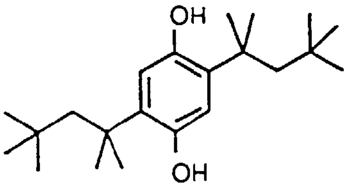
Coating Method 3: Photographic elements were prepared by coating a gel-subbed, polyethylene-coated paper support with a photosensitive layer containing a silver chloride emulsion at 0.172 g Ag/m^2 (or 0.2865 for 4-equivalent couplers), gelatin at 1.238 g/m^2, and a magenta image coupler indicated below at 0.38 mmol/m^2 dispersed in an equal weight of tricresyl phosphate. Each coupler dispersion also contained the following addenda (weight percent of coupler): Addendum-3 (48%), Addendum-4 (29%), Addendum-5 (32%), Addendum-6 (16%). The photosensitive layer was overcoated with a protective layer containing gelatin at 1.08 g/m^2 and bisvinylsulfonylmethyl ether hardener at 2 weight percent based on total gelatin.

Coating Method 4 (2-Equivalent Couplers): Photographic elements were prepared by coating a gel-subbed, polyethylene-coated paper support with a photosensitive layer containing a silver chloride emulsion at 0.172 g Ag/m^2, gelatin at 1.615 g/m^2, and a magenta image coupler indicated below at 0.329 mmol/m^2 dispersed in the following addenda (weight percent of coupler):tricresyl phosphate (100%), Addendum-5 (116.7%), and Addendum-6 (16.7%). The photosensitive layer was overcoated with (1) an ultraviolet-absorbing layer containing gelatin at 1.33 g/m^2, 2-(2H-benzotriazol-2-yl)-2,4-bis-(1,1-dimethylpropyl)phenol at 0.732 g/m^2 and 2-(5-chloro-2H-benzotriazol-2-yl)-4-methyl-6-t-butyl)phenol at 0.129 g/m^2, and (2) a protective layer containing gelatin at 1.40 g/m^2 and bisvinylsulphonylmethyl ether hardener at 1.77 weight percent based on total gelatin. The levels of coupler and silver were chosen to approximate the sensitometry of the 4-equivalent check coupler.

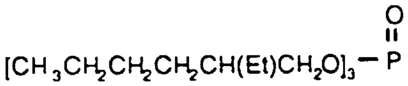
Addendum-1:



Addendum-2:

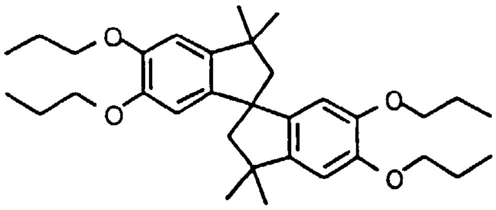


Addendum-3: (Compound No. I-1 in U.S. 4,217,410)

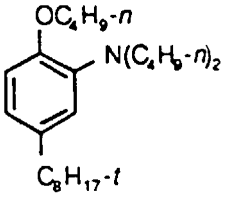


$$[CH_3CH_2CH_2CH_2CH(Et)CH_2O]_3-\overset{\overset{O}{\|}}{P}$$

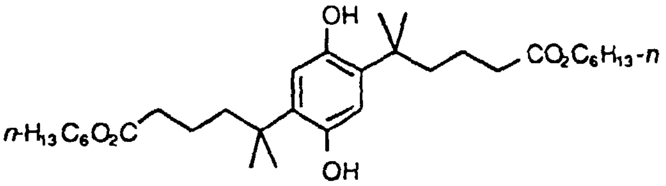
Addendum-4: (Compound No. 21 in U.S. 4,360,589)



Addendum-5: (Compound No. II-10 in EP 81,768)



Addendum-6: (Compound No. 104 in EP 69,070)



Process Method 1: Samples of each element were imagewise exposed through a graduated-density test object, processed in color developer 1 at 33°C for 3.25 minutes in the color developer, 1.5 minutes in the bleach-fix bath, washed and dried.

Process Method 2: Samples of each element were imagewise exposed through a graduated density test object, then processed in color developer 2 at 35°C (45 seconds in a color developer, 45 seconds in the bleach-fix bath of Examples 1-3) washed and dried.

Color Developer 1 (pH 10.08)	
Triethanolamine	11 mL
Benzyl alcohol	14.02 mL
Lithium chloride	2.0 g
Potassium bromide	0.6 g
Hydroxylamine sulfate	3.2 g
Potassium sulfite (45% solution)	2.8 mL
1-Hydroxyethylidene-1,1-di-phosphonic acid (60%)	0.8 mL
4-Amino-3-methyl-N-ethyl-N-(β-methanesulfonamido) ethylaniline sesquisulfate hydrate	4.35 g
Potassium carbonate (anhydrous)	28 g
Stilbene whitening agent	0.6 g
Surfactant	1 mL
Water to make	1.0 L

Color Developer 2 (pH 10.04)	
Triethanolamine	12.41 g
Lithium sulfate	2.70 g
N, N-Diethylhydroxylamine (85% solution)	5.40 g
1-Hydroxyethylidene-1, 1-di-phosphonic acid (60%)	1.16 g
4-Amino-3-methyl-N-ethyl-N-(β-methanesulfonamido) ethylanilinesesquisulfate hydrate	5.00 g
Potassium carbonate (anhydrous)	21.16 g
Potassium bicarbonate	2.79 g
Potassium chloride	1.60 g
Potassium bromide	7.0 mg
Stilbene whitening agent	2.30 g
Surfactant	1 mL
Water to make	1.0 L

Bleach-Fix Bath (pH 6.8)	
Ammonium thiosulfate	104 g
Sodium hydrogen sulfite	13 g
Ferric ammonium ethylenediamine tetraacetic acid (EDTA)	65.5 g
EDTA	6.56 g
Ammonium hydroxide (28%)	27.9 mL
Water to make	1 L

Example 3

Hue - The spectral characteristics (λmax) for the 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline dyes of the representative couplers are summarized in Table V. It is clearly evident that the dye hues of M-1 through M-6 are bathochromic relative to the dye hue obtained from the comparison couplers. Bathochromic dye hues are desirable for better color reproduction.

Table V.

Spectral Characteristics of the Magenta Dyes				
Coupler	**λmax (nm)**	**Coating Method**	**Process Method**	**Type**
C-1	536	3	2	Check
C-2	536	3	2	Check

Table V. (continued)

Spectral Characteristics of the Magenta Dyes				
Coupler	**λmax (nm)**	**Coating Method**	**Process Method**	**Type**
C-6	537	2	1	Check
C-7	537	3	2	Check
C-8	536	3	2	Check
C-9	536	2	1	Check
C-10	539	2	1	Check
M-1	543	2	1	Invention
M-2	542	2	1	Invention
M-3	542	2	1	Invention
M-4	543	4	2	Invention
M-5	543	4	2	Invention
M-6	543	4	2	Invention

Example 4

Thermal Stability: Comparison 4-equivalent couplers were coated by Method 1 and couplers of the invention were coated by Method 2. Both were processed by Method 1, and the data obtained after treatment under the specified conditions is listed in Table VI. It is clearly evident that couplers of the invention are much less prone to discoloration than the check couplers with the apparent exception of C-10. However, C-10 exhibits poor light stability as shown by Table VIII.

Table VI.

Thermal Stability of the Magenta Dyes[a,b]					
		Dmin Yellowing (Initial D=0)		Dye Fade (Initial D=1.0)	
Coupler	Type	Dry	Wet	Dry	Wet
CA-2 (Q=H)	Check	9	19	-8	0
CA-3 (Q=H)	Check	10	27	-15	6
A-1 (Q=H)	Check	14	30	-16	6
A-3 (Q=H)	Check	22	39	-9	11
C-10	Check	5	3	1	-1
M-1	Invention	7	7	3	2

[a] Dry Oven Conditions: 2 weeks at 77°C/15% relative humidity. [b] Wet Oven Conditions: 2 weeks at 60°C/70% relative humidity.

Example 5

The invention coupler M-2 and comparison coupler C-1 were coated using Method 3 and processed using Method 2. The processed coatings were exposed to heat and the results are tabulated below in Table VII. The large increases in density for the check coupler are indicative of the decomposition of a stable leuco-dye to give additional magenta dye upon heat treatment. The couplers of the invention do not form a stable leuco-dyes under these rapid access conditions. Therefore, couplers of the invention do not require Lippman fine grain silver halide for rapid machine processing, a distinct advantage over comparison coupler C-1.

Table VII.

Unwanted Formation of Stable Leuco-Dyes[a,b]					
		1 Week Fade (Initial D=1.7)		2 Week Fade (Initial D=1.7)	
Coupler	Type	Dry	Wet	Dry	Wet
C-1	Check	33	34	31	32

[a] Dry Oven Conditions: 77°C/15% relative humidity.

b Wet Oven Conditions: 60°C/70% relative humidity.

Table VII. (continued)

Unwanted Formation of Stable Leuco-Dyes[a,b]					
		1 Week Fade (Initial D=1.7)		2 Week Fade (Initial D=1.7)	
Coupler	Type	Dry	Wet	Dry	Wet
M-2	Invention	2	5	2	4

[a] Dry Oven Conditions: 77°C/15% relative humidity.
[b] Wet Oven Conditions: 60°C/70% relative humidity.

Example 6

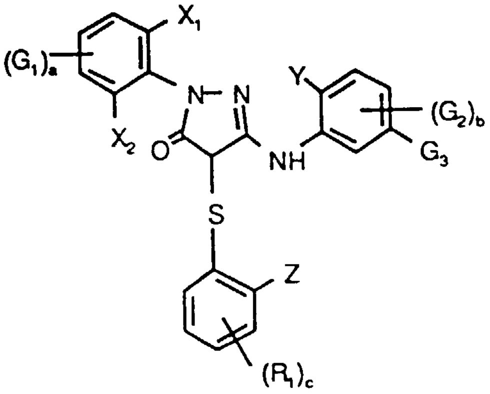
The invention coupler M-1 and comparison coupler C-10 were coated by Method 2 and processed using Method 1. The processed coatings were exposed to 50 Klux light though a Wratten 2B filter for 2 weeks and the results are tabulated below. As shown in Table VIII, the invention coupler shows only a small amount of photolytic yellowing, while the comparison coupler shows a very large amount of yellowing.

Table VIII.

Unwanted Photolytic Yellowing[a,b]		
Coupler	Type	2 Week Printout (Initial D=0.0)
C-10	Check	0.08
M-1	Invention	0.02

Claims

1. A photographic element comprising at least one photosensitive silver halide emulsion layer having associated therewith a 5-pyrazolone photographic coupler represented by the formula:



wherein:

a) substituents X_1, X_2, Y, G_1, and G_2 are individually selected from the group consisting of halogen, alkyl, alkoxy, aryloxy, acylamino, alkylthio, arylthio, sulfonamido, sulfamoyl, sulfamido, carbamoyl, diacylamino, alkoxycarbonyl, aryloxycarbonyl, alkoxysulfonyl, aryloxysulfonyl, alkylsulfonyl, arylsulfonyl, alkylsulfinyl, arylsulfinyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, acyloxy, nitro, trifluoromethyl and carboxy and, in the case of X_1, X_2, and Y, hydrogen;
b) a, b, and c are individually integers form 0 to 3 provided that "a" cannot be an integer which, combined with the selection of X_1 and X_2, allows the number of chloride substituents on the ring containing G_1 to exceed 3;
c) G_3 is selected from the group consisting of hydrogen, halogen, acylamino, sulfonamido, sulfamido, carbamoyl, diacylamino, alkoxycarbonyl, aryloxycarbonyl, alkoxysulfonyl, aryloxysulfonyl, alkylsulfonyl, arylsulfonyl, alkylsulfinyl, arylsulfinyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, acyloxy, trifluoromethyl and carboxyl;

d) R_1 is selected from the group consisting of G_1 and hydroxyl;
e) Z is an alkyl group containing at least 3 carbon atoms; and
f) the sum of the sigma values for X_1, X_2, Y, G_1, G_2, and G_3 is at least 1.3.

2. The element of Claim 1 wherein the substituents X_1, X_2, Y, G_1, G_2, are individually selected from the group consisting of chloride, fluoride, acylamino, sulfonamido, sulfamoyl, carbamoyl, alkoxycarbonyl, aryloxycarbonyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonylamino, aryloxycarbonylamino, alkylureido, arylureido, and trifluoromethyl.

3. The element of Claim 1 wherein X_1, X_2 and Y are chloride.

4. The element of Claim 3 wherein G_1 and G_2 are individually selected from the group consisting of chloride, fluoride, acylamino, sulfonamido, sulfamoyl, carbamoyl, alkoxycarbonyl, aryloxycarbonyl, alkylsulfonyl, arylsulfonyl and trifluoromethyl.

5. The element of Claim 1 wherein Z is an alkyl group of not more that 30 carbon atoms.

6. The element of Claim 5 wherein Z contains less than 20 carbon atoms.

7. The element of Claim 5 wherein Z is a branched chain alkyl group.

8. The element of Claim 1 wherein the sum of the carbon atoms in Z and R_1 totals at least six.

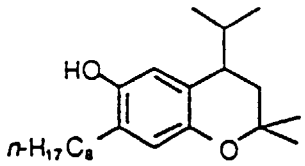
9. The element of Claim 1 wherein G_1 is para to the pyrazolone ring.

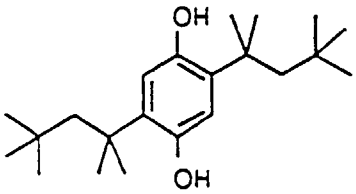
10. The element of Claim 1 wherein c is at least 1 and wherein R_1 is an alkyl group of at least 3 carbon atoms.

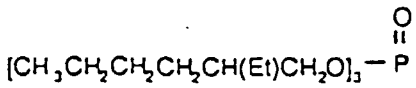
11. The element of Claim 10 wherein both Z and R_1 are branched chain alkyl groups.

12. The element of Claim 1 wherein the substituents on the arylthio group are free of alkoxy groups.

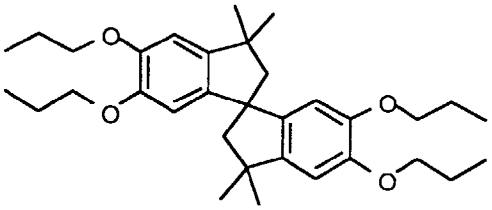
13. The element of Claim 1 additionally containing at least one addendum having a structure selected from the following:

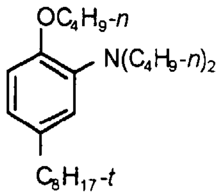


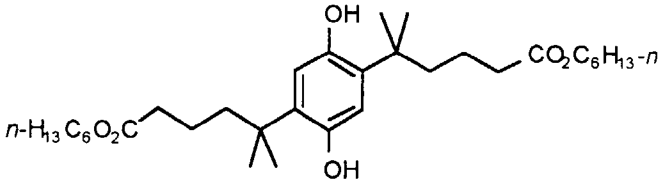




$$[CH_3CH_2CH_2CH_2CH(Et)CH_2O]_3-\overset{\overset{O}{\|}}{P}$$







14. The element of Claim 1 wherein the sum of the sigma values for X_1, X_2, Y, G_1, G_2, and G_3 is at least 1.4.

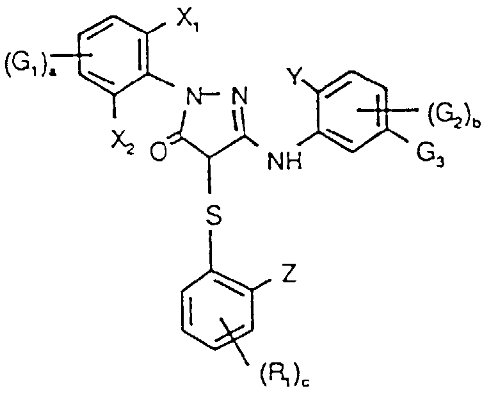
15. The element of Claim 1 wherein the photographic element additionally comprises a layer of magnetic particles.

16. The element of Claim 15 additionally comprising masking material which is yellow in unexposed areas following development.

17. A process of forming a photographic image in a photographic element as defined in claim 1, which comprises developing the exposed element with a color developing agent.

Patentansprüche

1. Photographisches Element mit mindestens einer photosensitiven Silberhalogenidemulsionsschicht, der ein photographischer 5-Pyrazolonkuppler zugeordnet ist, der durch die Formel dargestellt wird:



worin bedeuten:

a) die Substituenten X_1, X_2, Y, G_1 und G_2 sind einzeln ausgewählt aus der Gruppe bestehend aus Halogen, Alkyl, Alkoxy, Aryloxy, Acylamino, Alkylthio, Arylthio, Sulfonamido, Sulfamoyl, Sulfamido, Carbamoyl, Diacylamino, Alkoxycarbonyl, Aryloxycarbonyl, Alkoxysulfonyl, Aryloxysulfonyl, Alkylsulfonyl, Arylsulfonyl, Alkylsulfinyl, Arylsulfinyl, Alkoxycarbonylamino, Aryloxycarbonylamino, Alkylureido, Arylureido, Acyloxy, Nitro, Trifluoromethyl und Carboxy und im Falle von X_1, X_2 und Y Wasserstoff;

b) a, b und c sind einzeln Zahlen von 0 bis 3, wobei gilt, daß "a" keine Zahl sein kann, die, kombiniert mit der Auswahl von X_1 und X_2, es ermöglicht, daß die Anzahl von Chlorid-Substituenten am Ring, der G_1 aufweist, 3 überschreitet;

c) G_3 ist ausgewählt aus der Gruppe bestehend aus Wasserstoff, Halogen, Acylamino, Sulfonamido, Sulfamido, Carbamoyl, Diacylamino, Alkoxycarbonyl, Aryloxycarbonyl, Alkoxysulfonyl, Aryloxysulfonyl, Alkylsulfonyl, Arylsulfonyl, Alkylsulfinyl, Arylsulfinyl, Alkoxycarbonylamino, Aryloxycarbonylamino, Alkylureido, Arylureido, Acyloxy, Trifluoromethyl und Carboxyl;

d) R_1 ist ausgewählt aus der Gruppe bestehend aus G_1 und Hydroxyl;

e) Z ist eine Alkylgruppe mit mindestens 3 Kohlenstoffatomen; und

f) die Summe der Sigma-Werte für X_1, X_2, Y, G_1, G_2 und G_3 beträgt mindestens 1,3.

2. Element nach Anspruch 1, in dem die Substituenten X_1, X_2, Y, G_1, G_2 einzeln ausgewählt sind aus der Gruppe bestehend aus Chlorid, Fluorid, Acylamino, Sulfonamido, Sulfamoyl, Carbamoyl, Alkoxycarbonyl, Aryloxycarbonyl, Alkylsulfonyl, Arylsulfonyl, Alkoxycarbonylamino, Aryloxycarbonylamino, Alkylureido, Arylureido und Trifluoromethyl.

3. Element nach Anspruch 1, in dem X_1, X_2 und Y für Chlorid stehen.

4. Element nach Anspruch 3, in dem G_1 und G_2 einzeln ausgewählt sind aus der Gruppe bestehend aus Chlorid, Fluorid, Acylamino, Sulfonamido, Sulfamoyl, Carbamoyl, Alkoxycarbonyl, Aryloxycarbonyl, Alkylsulfonyl, Arylsulfonyl und Trifluoromethyl.

5. Element nach Anspruch 1, in dem Z eine Alkylgruppe mit nicht mehr als 30 Kohlenstoffatomen ist.

6. Element nach Anspruch 5, in dem Z weniger als 20 Kohlenstoffatome enthält.

7. Element nach Anspruch 5, in dem Z eine verzweigtkettige Alkylgruppe ist.

8. Element nach Anspruch 1, in dem die Summe der Kohlenstoffatome in Z und R_1 insgesamt mindestens 6 beträgt.

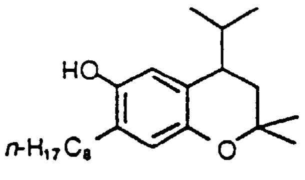
9. Element nach Anspruch 1, in dem G_1 sich in para-Stellung zu dem Pyrazolonring befindet.

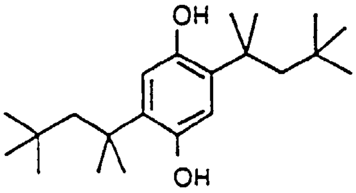
10. Element nach Anspruch 1, in dem c mindestens 1 ist, und in dem R_1 eine Alkylgruppe mit mindestens 3 Kohlenstoffatomen darstellt.

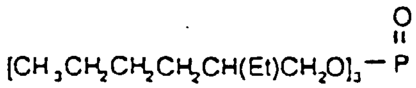
11. Element nach Anspruch 10, in dem sowohl Z als auch R_1 verzweigtkettige Alkylgruppen sind.

12. Element nach Anspruch 1, in dem die Substituenten an der Arylthiogruppe frei von Alkoxygruppen sind.

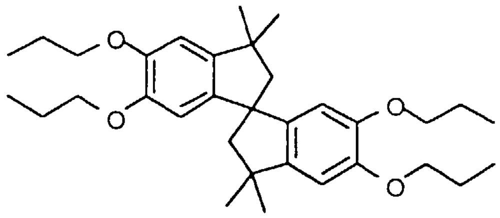
13. Element nach Anspruch 1, das zusätzlich mindestens einen Zusatz mit einer Struktur, ausgewählt aus den folgenden Strukturen, enthält:

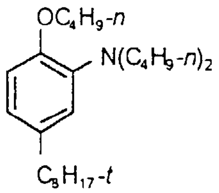


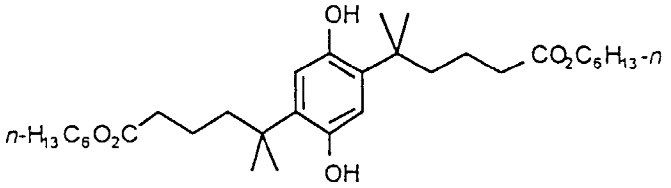




$$[CH_3CH_2CH_2CH_2CH(Et)CH_2O]_3-P=O$$







14. Element nach Anspruch 1, in dem die Summe der Sigma-Werte für X_1, X_2, Y, G_1, G_2 und G_3 mindestens 1,4 beträgt.

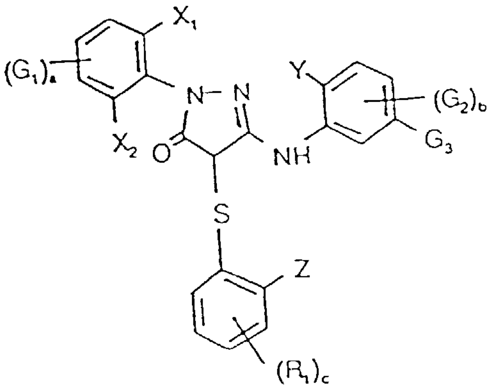
15. Element nach Anspruch 1, das zusätzlich eine Schicht von magnetischen Teilchen aufweist.

16. Element nach Anspruch 15, das zusätzlich ein Maskierungsmaterial aufweist, das in nicht-exponierten Bereichen nach der Entwicklung gelb ist.

17. Verfahren zur Herstellung eines photographischen Bildes in einem photographischen Element wie in Anspruch 1 definiert, das umfaßt die Entwicklung des exponierten Elementes mit einer Farbentwicklerverbindung.

Revendications

1. Elément photographique comprenant au moins une couche d'émulsion photosensible aux halogénures d'argent à laquelle est associé un coupleur photographique du type 5-pyrazolone représenté par la formule :



où :

a) les substituants X_1, X_2, Y, G_1 et G_2 sont choisis séparément dans le groupe constitué d'un halogène et des groupes alkyle, alkoxy, aryloxy, acylamino, alkylthio, arylthio, sulfonamido, sulfamoyle, sulfamido, carbamoyle, diacylamino, alkoxycarbonyle, aryloxycarbonyle, alkoxysulfonyle, aryloxysulfonyle, alkylsulfonyle, arylsulfonyle, alkylsulfinyle, arylsulfinyle, alkoxycarbonylamino, aryloxycarbonylamino, alkyluréido, aryluréido, acyloxy, nitro, trifluorométhyle et carboxy et, dans le cas de X_1, X_2 et Y, de l'hydrogène ;
b) a, b et c sont séparément des nombres entiers compris entre 0 et 3, à condition que "a" ne puisse pas être un nombre entier qui, combiné à la sélection de X_1 et X_2, permet au nombre de substituants chlorure sur le noyau contenant G_1 de dépasser 3 ;
c) G_3 est choisi dans le groupe constitué de l'hydrogène, d'un halogène et des groupes acylamino, sulfonamido, sulfamido, carbamoyle, diacylamino, alkoxycarbonyle, aryloxycarbonyle, alkoxysulfonyle, aryloxysulfonyle, alkylsulfonyle, arylsulfonyle, alkylsulfinyle, arylsulfinyle, alkoxycarbonylamino, aryloxycarbonylamino, alkyluréido, aryluréido, acyloxy, trifluorométhyle et carboxyle ;
d) R_1 est choisi dans le groupe constitué de G_1 et du groupe hydroxyle ;
e) Z est un groupe alkyle contenant au moins 3 atomes de carbone ; et
f) la somme des valeurs sigma pour X_1, X_2, Y, G_1, G_2 et G_3 est au moins égale à 1,3.

2. Elément photographique selon la revendication 1, dans lequel les substituants X_1, X_2, Y, G_1 et G_2 sont choisis séparément dans le groupe constitué des groupes chlorure, fluorure, acylamino, sulfonamido, sulfamoyl, carbamoyle, alkoxycarbonyle, aryloxycarbonyle, alkylsulfonyle, arylsulfonyle, alkoxycarbonylamino, aryloxycarbonylamino, alkyluréido, aryluréido et trifluorométhyle.

3. Élément photographique selon la revendication 1, dans lequel X_1, X_2 et Y représentent un chlorure.

4. Elément photographique selon la revendication 3, dans lequel G_1 et G_2 sont choisis séparément dans le groupe constitué des groupes chlorure, fluorure, acylamino, sulfonamido, sulfamoyle, carbamoyle, alkoxycarbonyle, aryloxycarbonyle, alkylsulfonyle, arylsulfonyle et trifluorométhyle.

5. Elément photographique selon la revendication 1, dans lequel Z est un groupe alkyle ne contenant pas plus de 30 atomes de carbone.

6. Elément photographique selon la revendication 5, dans lequel Z contient moins de 20 atomes de carbone.

7. Elément photographique selon la revendication 5, dans lequel Z est un groupe alkyle à chaîne ramifiée.

8. Elément photographique selon la revendication 1, dans lequel la somme des atomes de carbone contenus dans Z et R_1 est au moins égale à six.

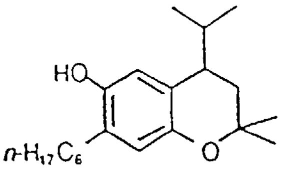
9. Elément photographique selon la revendication 1, dans lequel G_1 est en position para par rapport au cycle pyrazolone.

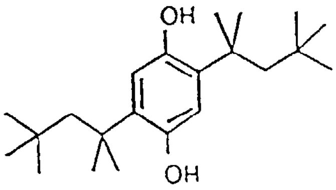
10. Elément photographique selon la revendication 1, dans lequel c est au moins égal à 1 et dans lequel R_1 est un groupe alkyle contenant au moins 3 atomes de carbone.

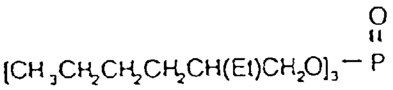
11. Elément photographique selon la revendication 10, dans lequel Z et R_1 sont tous deux des groupes alkyle à chaîne ramifiée.

12. Elément photographique selon la revendication 1, dans lequel les substituants sur le groupe arylthio sont exempts de groupes alkoxy.

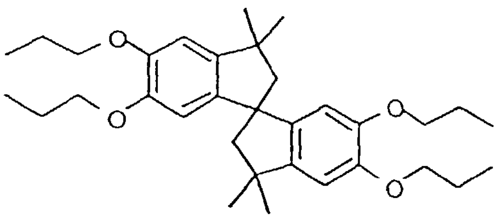
13. Elément photographique selon la revendication 1, contenant aussi au moins un additif ayant une structure choisie parmi les suivantes :

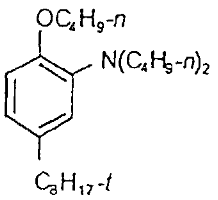


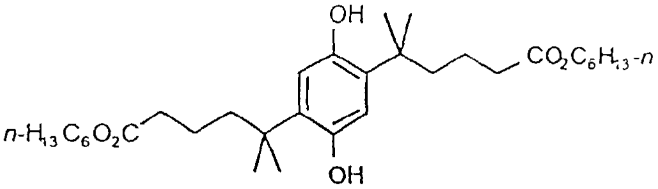




$$[CH_3CH_2CH_2CH_2CH(Et)CH_2O]_3-\overset{O}{\overset{\|}{P}}$$







14. Elément photographique selon la revendication 1, dans lequel la somme des valeurs sigma pour X_1, X_2, Y, G_1, G_2 et G_3 est au moins égale à 1,4.

15. Elément photographique selon la revendication 1, dans lequel l'élement photographique comprend aussi une couche de particules magnétiques.

16. Elément photographique selon la revendication 15, comprenant aussi un matériau de masquage qui, après développement, est jaune dans les zones non exposées.

17. Procédé pour former une image photographique dans un élément photographique tel que défini dans la revendication 1, qui comprend le développement de l'élément photographique exposé à l'aide d'un développateur chromogène.